



Europäisches Patentamt
 European Patent Office
 Office européen des brevets



(11) EP 0 769 505 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent: 10.05.2000 Bulletin 2000/19
 (51) Int Cl.7: C08F 210/06, C08F 210/16

(21) Application number: 96120158.9

(22) Date of filing: 21.12.1989

(54) Olefin copolymers and processes for preparing same

Olefin copolymere und Verfahren zur Herstellung davon
 Copolymères oléfiniques et leurs procédés de préparation

<p>(84) Designated Contracting States: DE FR GB IT NL</p> <p>(30) Priority: 26.12.1988 JP 32873288 26.12.1988 JP 32873488 26.12.1988 JP 32873188 24.01.1989 JP 11459689 21.07.1989 JP 18904489</p> <p>(43) Date of publication of application: 23.04.1997 Bulletin 1997/17</p> <p>(60) Divisional application: 99105417.2 / 0 955 321 99105447.9 / 0 955 322</p> <p>(62) Document number(s) of the earlier application(s) in accordance with Art. 76 EPC: 95202089.9 / 0 685 498 90900353.5 / 0 495 099</p> <p>(73) Proprietor: MITSUI CHEMICALS, INC. Tokyo (JP)</p> <p>(72) Inventors: • Tsutsui, Toshiyuki Waki-cho, Kuga-gun, Yamaguchi (JP)</p>	<p>• Toyota, Akinori Waki-cho, Kuga-gun, Yamaguchi (JP)</p> <p>(74) Representative: Cresswell, Thomas Anthony J.A. KEMP & CO. 14 South Square Gray's Inn London WC1R 5LX (GB)</p> <p>(56) References cited: EP-A- 0 260 999 EP-A- 0 263 718 DE-A- 2 637 990 DE-A- 2 637 991 GB-A- 2 052 532 US-A- 4 761 462</p> <p>• PATENT ABSTRACTS OF JAPAN vol. 11, no. 349 (C-456) [2796], 14 November 1987 & JP 62 119212 A (MITSUI PETROCHEMICAL INDUSTRIES LTD.), 30 May 1987, • PATENT ABSTRACTS OF JAPAN vol. 12, no. 450 (C-547) [3297], 25 November 1988 & JP 63 175004 A (MITSUI PETROCHEMICAL INDUSTRIES LTD.), 19 July 1988, • PATENT ABSTRACTS OF JAPAN vol. 12, no. 444 (C-545) [3291], 22 November 1988 & JP 63 168407 A (SHOWA DENKO K.K.), 12 July 1988,</p>
--	---

EP 0 769 505 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

5 [0001] This invention relates to propylene random copolymers and process for preparing the same and more particularly to propylene random copolymers having low melting points in comparison with conventionally known propylene random copolymers and, in particular, excellent heat-sealing properties and anti-block properties, and to a process for preparing the same.

10 [0002] Polypropylene has wide applications in the field of plastics because of its excellent physical properties. For example, polypropylene is widely used as packaging film material. In the applications of the type, however, because of its relatively high melting point, polypropylene is generally copolymerized with ethylene or α -olefins of 4 to 20 carbon atoms in order to improve the heat-sealing properties at low temperature, and is used in the form of a propylene/ α -olefin copolymer.

15 [0003] Packaging films formed from these known propylene/ α -olefin copolymers still do not have sufficient heat-sealing properties, though they have excellent transparency and scratch resistance in comparison with those formed from low density polyethylene, and accordingly it is hoped that propylene/ α -olefin copolymers having excellent heat-sealing properties even at lower temperatures will be obtained.

[0004] It is well known that the above-mentioned propylene/ α -olefin random copolymers may be improved in heat-sealing properties by increasing the proportion of ethylene or α -olefin of 4 to 20 carbon atoms to propylene in the copolymer. However, if the proportion of ethylene or α -olefin of 4 to 20 carbon atoms is increased in the copolymerization, the resulting propylene/ α -olefin copolymer increases in amount of the solvent-soluble component, whereby the resultant copolymer come to be poor in anti-blocking properties and also in stiffness.

20 [0005] Such propylene/ α -olefin random copolymers excellent in heat-sealing properties, anti-block properties and stiffness as mentioned above are available only when they have a low melting point in spite of the fact that the proportion of α -olefin in the copolymer is small.

25 [0006] Japanese Patent L-O-P Publ. No. 130314/1986 discloses polypropylene having a high isotacticity obtained by polymerization of propylene in the presence of a catalyst system comprising a sterically fixed zirconium-chelate compound and aluminoxane.

30 [0007] J. Am. Chem. Soc., 109, 6544 (1987) discloses the formation of a high molecular weight isotactic polypropylene obtained by polymerization of propylene in the presence of a catalyst system comprising ethylenebis(indenyl) hafnium dichloride or its hydride and aluminoxane, said isotactic polypropylene having a narrow molecular weight distribution ($\overline{M}_w/\overline{M}_n$) of 2.1-2.4.

[0008] Japanese Patent L-O-P Publ. No. 142005/1987 discloses a stereoblock polypropylene having $\overline{M}_w/\overline{M}_n$ of 5.0-14.9 obtained by polymerization of propylene in the presence of a catalyst system comprising tetramethylethylenebis (cyclopentadienyl) titanium chloride and aluminoxane. The polypropylene thus obtained has a short isotactic chain length and is a rubbery polymer.

35 [0009] EP-A-0263 718 discloses a propylene random copolymer composition comprising

- (I) 60 to 95% by weight of a propylene random copolymer, and
- (II) 5 to 40% by weight of a low-crystalline propylene random copolymer.

40 [0010] The present inventors have found that when propylene, ethylene and α -olefins of 4-20 carbon atoms are copolymerized in the presence of an olefin polymerization catalyst composed of specific hafnium compounds and aluminoxane, there are obtained propylene/ethylene/ α -olefin copolymers which are narrow in molecular weight distribution and small in amount of the α -olefin copolymerized therewith, but are low in melting point in comparison with conventionally known propylene random copolymers.

45 [0011] A further object of the invention is to provide propylene ethylene/ α -olefin copolymers which are narrow in molecular weight distribution and small in amount of the α -olefin copolymerized therewith but have a low melting point and, moreover, which are excellent in heat-sealing properties and also excellent in anti-block properties and stiffness, and processes for preparing the same.

50 [0012] The present invention provides a propylene random copolymer comprising structural units (a) derived from propylene, structural units (b) derived from ethylene and structural units (c) derived from α -olefins of 4-20 carbon atoms, and having

- (i) the structural units (a) in an amount of 90 to 99 mol%, the structural units (b) in an amount of 0.5 to 9.5 mol% and the structural units (c) in an amount of 0.5 to 9.5 mol%,
- 55 (ii) an intrinsic viscosity $[\eta]$ as measured in decalin at 135°C of 0.5 to 6 dl/g,
- (iii) a melting point $[T_m]$, as measured by a differential scanning calorimeter falling within the range of

5 wherein P is the propylene content (mol%) present in the copolymer, and
(iv) a boiling trichloroethylene-insoluble content of less than 5% by weight.

10 **[0013]** The present invention also provides a process for preparing a propylene random copolymer as defined above, which process comprises copolymerizing propylene, ethylene and an α -olefin of 4 to 20 carbon atoms in the presence of a catalyst comprising

[A] a hafnium compound having as a ligand a multidentate compound in which at least two groups selected from among cycloalkadienyl groups or substituted groups thereof are linked together via ethylene groups, and
[B] organoaluminum oxy-compounds.

15 **[0014]** The present invention additionally provides a heat sealing agent comprising the propylene random copolymers defined above.

[0015] In the accompanying Figures:

[0016] Fig. 1 is an illustration of process for the preparation of the olefin copolymers of the present invention.

20 **[0017]** Figs. 2 to 4 are stepwise illustrative of the method of evaluation of heat-sealing properties of the propylene random copolymer of the present invention.

[0018] The process for the preparation of the propylene copolymers of the present invention is illustratively shown in Fig. 1

25 **[0019]** The composition of the copolymer is determined by measuring a spectrum of ^{13}C -NMR of a specimen obtained by dissolving about 200 mg of the copolymer in 1 ml of hexachlorobutadiene in a test tube of 10 mm ϕ under the conditions of a measurement temperature of 120°C, measurement frequency of 25.05 MHz, spectrum width of 1500 Hz, pulse repetition time of 4.2 sec. and pulse width of 6 sec.

[0020] The ratio (\bar{M}_w/\bar{M}_n) obtained in the invention was determined by the following procedure in accordance with Takeuchi, "Gel Permeation Chromatography," Maruzen, Tokyo.

30 (1) Using a standard polystyrene having a known molecular weight (a monodispersed polystyrene produced and sold by Toyo Soda K.K.), the molecular weight \bar{M} and GPC (Gel Permeation Chromatography) count of the sample are measured to prepare a correlation diagram calibration curve of the molecular weight \bar{M} and EV (Elution Volume). The concentration of the sample used is maintained at 0.02% by weight.

35 (2) A GPC chromatograph of the sample is taken by GPC measurement, and a number average molecular weight \bar{M}_n and weight average molecular weight \bar{M}_w , in terms of polystyrene, are calculated from the calibration curve mentioned in the above procedure (1) to obtain a value of \bar{M}_w/\bar{M}_n .

[0021] The conditions under which the sample is prepared, and the conditions under which GPC measurement is conducted are as follows:

40 [Preparation of sample]

[0022]

45 (a) The sample is put in an Erlenmeyer flask together with o-dichlorobenzene so that the same amounts to 0.1% by weight.

(b) The Erlenmeyer flask is heated to 140°C and stirred for about 30 minutes to dissolve the sample in the o-dichlorobenzene.

50 (c) The solution is subjected to GPC.

[GPC measurement conditions]

[0023] The measurement was conducted under the following conditions.

55 (a) Apparatus 150C-ALC/GPC manufactured by Waters Co.

(b) Column GMH Type manufactured by Toyo Soda K.K.

(c) Amount of sample 400 μl

(d) Temperature 140°C

(e) Flow rate 1 ml/min

[0024] The catalyst components [A] used in the invention are hafnium compounds having multidentate coordination compounds as ligands in which at least two groups selected from among cycloalkadienyl groups or substituted groups thereof, e.g. an indenyl group, substituted indenyl group and partially hydrated compounds thereof, are linked together via ethylene groups.

[0025] The above-mentioned hafnium compounds include, for example, the following compounds.

10 Ethylenebis(indenyl)dimethyl hafnium,
 Ethylenebis(indenyl)diethyl hafnium,
 Ethylenebis(indenyl)diphenyl hafnium,
 Ethylenebis(indenyl)methyl hafnium monochloride,
 Ethylenebis(indenyl)ethyl hafnium monochloride,
 Ethylenebis(indenyl)methyl hafnium monobromide,
 15 Ethylenebis(indenyl)hafnium dichloride,
 Ethylenebis(indenyl)hafnium dibromide,
 Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)dimethyl hafnium,
 Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)methyl hafnium monochloride,
 Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)hafnium dichloride,
 20 Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)hafnium dibromide,
 Ethylenebis(4-methyl-1-indenyl)hafnium dichloride,
 Ethylenebis(5-methyl-1-indenyl)hafnium dichloride,
 Ethylenebis(6-methyl-1-indenyl)hafnium dichloride,
 Ethylenebis(7-methyl-1-indenyl)hafnium dichloride,
 25 Ethylenebis(5-methoxy-1-indenyl)hafnium dichloride,
 Ethylenebis(2,3-dimethyl-1-indenyl)hafnium dichloride,
 Ethylenebis(4,7-dimethyl-1-indenyl)hafnium dichloride,
 Ethylenebis(4,7-dimethoxy-1-indenyl)hafnium dichloride.

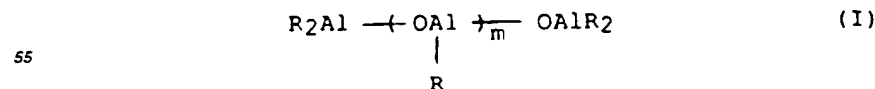
30 [0026] The above-mentioned hafnium compounds may contain small amounts of zirconium or titanium. In such a case, the content of zirconium or titanium is less than 1% by weight, preferably less than 0.7% by weight and especially less than 0.5% by weight.

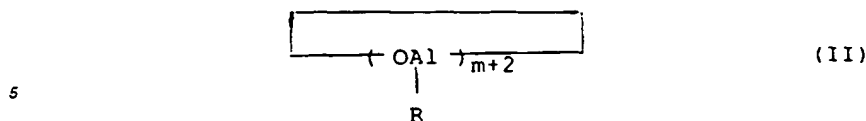
[0027] The hafnium catalyst components used in the present invention may include compounds obtained by treating the above-mentioned hafnium compounds with alkylsilylated silica gel. More particularly, said hafnium catalyst components may be hafnium compound solutions which are obtained, for example, by passing a solution of the above-mentioned hafnium compound in an organic solvent such as toluene through a column packed with an alkylsilylated silica gel, wherein said hafnium compound is brought into contact with the alkylsilylated silica gel.

[0028] The organic solvents used in that case are preferably aromatic hydrocarbons such as toluene, benzene and xylene. The alkylsilylated silica gel used may include those obtained by treating silica gel with dimethyl dichlorosilane, ethylmethyl dichlorosilane, trimethyl chlorosilane, trimethyl bromosilane, divinyl dichlorosilane, diethyl dichlorosilane or methylpropyl dichlorosilane. The hafnium concentration in the hafnium compound solution is usually from 1×10^{-5} to 5×10^{-3} mol/l, and the amount of the alkylsilylated silica gel used is usually 20-500 g per 1 mmol of the hafnium compound. The temperature at which the hafnium compound solution is brought into contact with the alkylsilylated silica gel is usually 0-50°C.

45 [0029] When the hafnium catalyst components obtained by treating the above-mentioned hafnium compounds with the alkylsilylated silica gel are used as the catalyst components [A], propylene copolymers having excellent transparency are obtained.

[0030] The catalyst components [B] used in the process of the present invention are organoaluminum oxy-compounds. The organoaluminum oxy-compounds used as the catalyst components may be benzene-soluble aluminoxanes of formula (I) or (II).





10 wherein each R may be the same or different and is a hydrocarbon group such as methyl, ethyl, propyl or butyl, preferably methyl or ethyl and especially methyl, and m is an integer of at least 2, preferably at least 5. The above-mentioned aluminoxanes may be prepared, for example, by the procedures exemplified below.

- 15 (1) A procedure which comprises reacting a suspension in a hydrocarbon medium of a compound containing water of absorption or a salt containing water of crystallization, for example, magnesium chloride hydrate, copper sulfate hydrate, aluminumsulfate hydrate, nickel sulfate hydrate or cerous chloride hydrate, with a trialkylaluminum.
- (2) A procedure which comprises reacting trialkylaluminum directly with water, water vapor or ice in a medium such as benzene, toluene, ethyl ether and tetrahydrofuran.

- 20 **[0031]** The aluminoxanes as illustrated above may contain small amounts of organometallic components.
- [0032]** Further, the organoaluminum oxy-compounds used in the present invention may be those which are insoluble in benzene. The benzene-insoluble organoaluminum oxy-compounds are illustrated hereinafter.
- [0033]** The benzene-insoluble organoaluminum oxy-compounds used in the invention may be prepared by (i) reaction of organoaluminum compounds with water or (ii) reaction of solutions of aluminoxane, for example, hydrocarbon solutions thereof, with water or active hydrogen-containing compounds.
- 25 **[0034]** The benzene-insoluble organoaluminum oxy-compounds are considered to have alkyloxyaluminum units of formula



35 wherein R¹ is hydrocarbon of 1 ~ 12 carbon atoms and the Al component soluble in benzene at 60°C is present in an amount, in terms of Al atom, of less than 10%, preferably less than 5% and especially less than 2%. Thus they are insoluble or sparingly soluble in benzene.

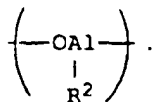
40 **[0035]** The solubility in benzene of the organoaluminum oxy-compounds is determined by suspending the organoaluminum oxy-compound equivalent to Al of 100 mg atom in 100 ml of benzene, stirring the suspension at 60°C for 6 hours, filtering the thus treated suspension at a temperature elevated to 60°C using a G-5 glass filter equipped with a jacket, washing 4 times the solids portion separated on the filter with 50 ml of benzene kept at 60°C and then measuring the amount of Al atoms (x mmol) present in the total filtrate.

45 **[0036]** In the alkyloxyaluminum units mentioned above, R¹ is, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, pentyl, hexyl, octyl, decyl, cyclohexyl or cyclooctyl. Among these, preferred are methyl and ethyl, particularly methyl.

[0037] In addition to the alkyloxyaluminum units of formula



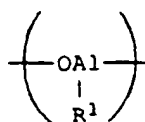
55 the benzene-insoluble organoaluminum oxy-compounds may contain oxyaluminum units of the formula



5

In the above-mentioned formulae, R¹ is as defined previously, R² is hydrocarbon of 1 ~ 12 carbon atoms, alkoxy of 1 ~ 12 carbon atoms aryloxy of 6 ~ 20 carbon atoms, hydroxyl, halogen or hydrogen, and R¹ and R² are different from each other. In that case, the benzene-insoluble organoaluminum oxy-compounds are preferably those containing the alkoxyaluminum units

10



15

in a proportion of at least 30 mol%, preferably at least 50 mol% and especially at least 70 mol%.

[0038] The organoaluminum compounds (i) used for preparing such benzene-insoluble organoaluminum oxy-compounds as mentioned above are those of formula R¹_nAlX_{3-n} wherein R¹ is hydrocarbon of 1 to 12 carbon atoms, X is halogen, alkoxy of 1 to 12 carbon atoms, aryloxy of 6 to 20 carbon atoms or hydrogen, and n is 2 or 3.

[0039] Such organoaluminum compounds (i) as mentioned above include trialkylaluminum such as trimethylaluminum, triethylaluminum, tripropylaluminum, triisopropylaluminum, tri-n-butylaluminum, tri-sec-butylaluminum, tri-tert-butylaluminum, tripentylaluminum, trihexylaluminum, trioctylaluminum, tridecylaluminum, tricyclohexylaluminum and tricyclooctylaluminum; dialkylaluminum halides such as dimethylaluminum chloride, dimethylaluminum bromide, diethylaluminum chloride, diethylaluminum bromide, and diisobutylaluminum chloride; dialkylaluminum hydrides such as diethylaluminum hydride and diisobutylaluminum hydride; dialkylaluminum alkoxides such as dimethylaluminum methoxide and diethylaluminum ethoxide; and dialkylaluminum aryloxides such as diethylaluminum phenoxide. Of these organoaluminum compounds, preferred are those of the above-mentioned formula in which R¹ is alkyl and X is chlorine, and particularly preferred is trialkylaluminum.

[0040] In this connection, isoprenylaluminum of the general formula (i-C₄H₉)_xAl_y(C₅H₁₀)_z wherein x, y and z are each positive integer, and z ≥ 2x may also used as the organoaluminum compound (i).

[0041] The organoaluminum compounds (i) as illustrated above may be used either singly or in combination.

[0042] The active hydrogen-containing compounds (ii) used in preparing the benzene-insoluble organoaluminum oxy-compounds include alcohols such as methyl alcohol and ethyl alcohol, and diols such as ethylene glycol and hydroquinone.

[0043] When water is used in preparing the benzene-insoluble organoaluminum oxy-compounds, the water may be used after dissolving or suspending in hydrocarbon solvents such as benzene, toluene and hexane, ether solvents such as tetrahydrofuran, and amine solvents such as triethylamine, or may be used in the form of water vapor or ice. As the water, moreover, there may also be used water of crystallization of a salt such as magnesium chloride, magnesium sulfate, aluminum sulfate, copper sulfate, nickel sulfate, iron sulfate and cerrous chloride, or water of adsorption adsorbed to inorganic compounds such as silica, alumina and aluminum hydroxide or polymers.

[0044] As mentioned above, the benzene-insoluble organoaluminum oxy-compounds may be prepared by reaction of the organoaluminum compound (i) with water, or by reaction of a solution of aluminosane, for example, a hydrocarbon solution thereof, with water or the active hydrogen containing compound. In preparing the benzene-insoluble organoaluminum oxy-compound from the organoaluminum compound and water, the organoaluminum compound is brought into contact with water in a solvent, for example, a hydrocarbon solvent, and in that case, the water is added to the reaction system so that the organoaluminum atoms dissolved in the reaction system become less than 20% based on the total organoaluminum atom. In obtaining the benzene-insoluble organoaluminum oxy-compounds according to the procedure as mentioned above, it is desirable that the water is brought into contact with the organoaluminum compound in the proportion of 1 ~ 5 moles, preferably 1.5 ~ 3 moles of the water to 1 mole of the organoaluminum compound.

[0045] The above-mentioned reaction for forming the benzene-insoluble organoaluminum oxy-compounds is carried out in solvents, for example, hydrocarbon solvents. The solvents used include aromatic hydrocarbons such as benzene, toluene, xylene, cumene and cymene, aliphatic hydrocarbons such as butane, isobutane, pentane, hexane, octane, decane, dodecane, hexadecane and octadecane, alicyclic hydrocarbons such as cyclopentane, cyclooctane, cyclododecane and cyclododecane, such hydrocarbon solvents, for example, petroleum fractions, as gasoline, kerosine

55

and gas oil, halides of the above-mentioned aromatic hydrocarbons, aliphatic hydrocarbons and alicyclic hydrocarbons, especially chlorides and bromides thereof, and ethers such as ethyl ether and tetrahydrofuran. Among these hydrocarbon media as exemplified above, particularly preferred are aromatic hydrocarbons.

5 **[0046]** The concentration in terms of Al atom of the organoaluminum compound in the reaction system is desirably 1×10^{-3} to 5 gram atom/l preferably 1×10^{-2} to 3 gram atom/l, and the concentration in the reaction system of water such as water of crystallization is usually 1×10^{-3} to 20 mol/l, preferably 1×10^{-2} to 10 mol/l. In that case, it is desirable that the organoaluminum atoms dissolved in the reaction system are less than 20%, preferably less than 10% and especially in the range of from 0 to 5% based on the total organoaluminum atom.

10 **[0047]** Contact of the organoaluminum compound with water may be carried out, for example, by the following procedures.

(1) A procedure wherein a hydrocarbon solution of organoaluminum is brought into contact with a hydrocarbon solvent containing water.

15 (2) A procedure wherein water vapor is blown into a hydrocarbon solution of organoaluminum, thereby bringing the organoaluminum into contact with the water vapor.

(3) A procedure wherein a hydrocarbon solution of organoaluminum is mixed with a hydrocarbon suspension of a compound containing water of adsorption or a compound containing water of crystallization, thereby bringing the organoaluminum into contact with the water of adsorption or water of crystallization.

20 (4) A procedure wherein a hydrocarbon solution of organoaluminum is brought into contact with ice.

[0048] The above-mentioned reaction of the organoaluminum with water is usually carried out at a temperature of from -100 to 150°C , preferably -50 to 100°C and especially -30 to 80°C . The reaction time, though it may vary greatly depending upon the reaction temperature, is usually from 1 to 200 hours, preferably 2 to 100 hours.

25 **[0049]** In preparing the benzene-insoluble organoaluminum oxy-compounds from a solution of aluminosane and water or a active hydrogen-containing compound, the aluminosane present in the solution of aluminosane is brought into contact with water or the active hydrogen-containing compound.

30 **[0050]** The solution of aluminosane is a solution of aluminosane in a solvent such as used in forming the above-mentioned benzene-insoluble organoaluminum oxy-compounds, preferably aromatic hydrocarbons such as benzene and toluene. This solution may contain other components so long as they do not affect adversely the reaction between the aluminosane and water or the active hydrogen-containing compound.

35 **[0051]** The amount of water or the active hydrogen-containing compound used in the above-mentioned reaction is 0.1 to 5 moles, preferably 0.2 to 3 moles based on 1 gram atom of aluminum present in the solution of aluminosane. The concentration in the reaction system of aluminosane in terms of aluminum atom is usually 1×10^{-3} to 5 gram atom/l, preferably 1×10^{-2} to 3 gram atom/l, and the concentration in the reaction system of water is usually 2×10^{-4} to 5 mole/l, preferably 2×10^{-3} to 3 mole/l.

[0052] Taking, as an example, the reaction of the solution of aluminosane with water, said solution of aluminosane is brought into contact with water or the active hydrogen-containing compound, for example, by the following methods.

40 (1) A method which comprises bringing the solution of aluminosane into contact with a hydrocarbon solvent containing water.

(2) A method which comprises blowing water vapor into the solution of aluminosane, thereby bringing the aluminosane present in the solution of aluminosane into contact with the water vapor.

45 (3) A method which comprises mixing the solution of aluminosane with a hydrocarbon solution of a compound containing water of adsorption or a compound containing water of crystallization, thereby bringing the aluminosane present in the solution of aluminosane into contact with the water of adsorption or water of crystallization.

(4) A method which comprises bringing the solution of aluminosane into contact directly with water or ice.

[0053] The above-mentioned procedures may also be applied to the case wherein the active hydrogen-containing compound (ii) is used instead of water.

50 **[0054]** The reaction of the solution of aluminosane with water or the active hydrogen-containing compound as illustrated above may usually be carried out at a temperature of from -50° to 150°C , preferably 0° to 120°C and especially 20 to 100°C . The reaction temperature, though it may vary greatly depending upon the reaction temperature, is usually 0.5 to 300 hours, preferably about 1 ~ 150 hours.

55 **[0055]** In preparing the propylene copolymers by using the olefin polymerization catalysts as mentioned above, the concentration in the polymerization system of the hafnium compound in terms of hafnium atom is usually 10^{-8} to 10^{-2} gram atom/l, preferably 10^{-7} to 10^{-3} gram atom/l.

[0056] The above-mentioned organoaluminum oxy-compounds are desirably used in an amount in terms of aluminum atoms present in the reaction system of 10^{-4} to 10^{-1} gram atom/l, preferably 5×10^{-4} to 5×10^{-2} gram atom/l.

EP 0 769 505 B1

[0057] The polymerization temperature employed is from -50° to 150°C, preferably from 0° to 120°C.

[0058] The olefin polymerization mentioned above is usually carried out in the vapor phase or liquid phase. In liquid phase polymerization, the solvent used may be an inert hydrocarbon, or the olefin itself may also be used as the solvent.

[0059] The hydrocarbon used in that case includes aliphatic hydrocarbons such as butane, isobutane, pentane, hexane, heptane, octane, decane, dodecane, hexadecane and octadecane, alicyclic hydrocarbons such as cyclopentane, methylcyclopentane, cyclohexane and cyclooctane, aromatic hydrocarbons such as benzene, toluene and xylene, and petroleum fractions such as gasoline, kerosine and gas oil.

[0060] The polymerization pressure employed is usually from ordinary pressure to 100 kg/cm², preferably from ordinary pressure to 50 kg/cm², and the polymerization may be carried out batchwise, semi-continuously or continuously. The molecular weight of the resulting polymer may be modified by the addition of hydrogen and/or by regulation of the polymerization temperature employed.

[0061] The propylene random copolymers of the invention are random copolymers of propylene, ethylene and α -olefins of 4 to 20 carbon atoms. In the propylene random copolymers, the structural units (a) derived from propylene are present in an amount of 90 to 99 mol%, preferably 92 to 98 mol%, the structural units (b) derived from ethylene in an amount of 0.5 to 9.5 mol%, preferably 1 to 9 mol%, and the structural units (c) derived from α -olefin in an amount of 0.5 to 9.5 mol%, preferably 1 to 9 mol%. If the structural units (a) derived from propylene present in the said copolymers are less than 90 mol%, the copolymers tend to become poor in anti-blocking properties and stiffness. On the other hand, if the structural units (a) exceed 99 mol%, the copolymers tend to increase in melting point and become poor in heat-sealing properties.

[0062] α -olefins of 4 to 20 carbon atoms used herein include 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-octane, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene. Among these, particularly preferred is 1-butene.

[0063] The propylene random copolymers of the invention desirably have an intrinsic viscosity $[\eta]$ as measured in decalin at 135°C of 0.5 to 6 dl/g, preferably 1 to 5 dl/g. If this intrinsic viscosity is less than 0.5 dl/g, the copolymers tend to become poor in anti-blocking properties and toughness and, on the other hand, if said intrinsic viscosity exceeds 6 dl/g, the copolymers tend to become poor in moldability.

[0064] The propylene random copolymers of the invention have a melting point $[T_m]$ as measured by a differential scanning calorimeter falling within the range of

$$70 < T_m < 155 - 5.5 (100 - P),$$

preferably

$$90 < T_m < 150 - 5.5 (100 - P)$$

wherein P is the content (mol%) of propylene in the copolymer.

[0065] The melting point of the propylene random copolymers is 10 to 20°C lower than that of the known propylene/ α -olefin random copolymers when the amounts of ethylene and α -olefin copolymerized of the former are the same as those of the latter. Accordingly, films obtained from the second propylene random copolymers of the invention are excellent particularly in heat-sealing properties at low temperatures, and the films exhibit excellent heat-sealing properties even when they have small amounts of ethylene and α -olefin copolymerized, and hence they are excellent in anti-blocking properties and have excellent stiffness.

[0066] The molecular weight distribution (\bar{M}_w/\bar{M}_n) of the propylene random copolymers of the invention as obtained by gel permeation chromatography (GPC) is less than 3.5, preferably less than 3.0 and especially less than 2.5. As stated above, the propylene random copolymers of the invention have a narrow molecular weight distribution and, from this point, they have excellent anti-blocking properties.

[0067] The propylene random copolymers of the invention desirably have an amount of soluble portion in boiling n-pentane of less than 5% by weight, preferably less than 3% by weight and especially less than 2% by weight.

[0068] Furthermore, the propylene random copolymers of the invention desirably have an amount of insoluble portion in boiling trichloroethylene of less than 5% by weight, preferably less than 3% by weight and especially less than 1% by weight.

[0069] The amounts of the insoluble portion in boiling trichloroethylene and the soluble portion in boiling n-pentane were determined by such a manner that about 3 g of the finely pulverized specimen was extracted for 5 hours with 180 ml of each of the solvents in a cylindrical filter paper by using a Soxhlet's extractor, and the extraction residue was dried with a vacuum dryer until it reached a constant weight to obtain the weight thereof, whereby a difference in weight between the dried residue and the original specimen is calculated.

EP 0 769 505 B1

5 [0070] The propylene random copolymers of the present invention as illustrated above may be prepared by copolymerizing propylene, ethylene and α -olefins of 4 to 20 carbon atoms at a temperature of 40 to 100°C so that the structural units (a) derived from propylene are present in an amount of 90 to 99 mol% in the resulting copolymers, the structural units (b) derived from ethylene in an amount of 0.5 to 9.5 mol%, and the structural units (c) derived from α -olefin in an amount of 0.5 to 9.5 mol%, in the presence of catalysts formed from

[A] hafnium compounds having as ligands multidentate compounds in which at least two groups selected from among cycloalkadienyl groups or substituted groups thereof are linked together via ethylene groups, and
10 [B] organoaluminum oxy-compounds.

[0071] The propylene random copolymers of the invention have particularly excellent heat-sealing properties at low temperatures, and hence are used as heat-sealing agents.

15 [0072] The propylene copolymers of the invention have a low melting point in comparison with known propylene/ α -olefin random copolymers even when said propylene copolymers have a low α -olefin content, and hence they have excellent anti-blocking properties and stiffness. In the present invention, there are also provided processes for preparing these novel copolymers readily and efficiently.

[0073] The olefin polymerization catalysts described above exhibit high activities even when relatively small amounts of organoaluminum oxy-compounds are used therein, and by the use of said catalysts, olefin polymers large in molecular weight and narrow in molecular weight distribution and composition distribution are obtained.

20 [0074] The present invention is further illustrated below in the following Examples.

Example 1

(Preparation of methylaluminoxane)

25 [0075] Methylaluminoxane was prepared in accordance with the procedure described in Polymer Commun., 29, 180 (1988).

(Synthesis of ethylenebis(indenyl)hafnium dichloride)

30 [0076] A nitrogen-purged 200 ml glass flask was charged with 5.4 g of bis(indenyl)ethane [synthesized on the basis of Bull. Soc. Chim., 2954 (1967)] and 50 ml of THF, and the flask was cooled with stirring to -30° ~ -40°C. To the flask was added dropwise 31.5 ml of n-Bu Li (1.6M solution), stirred successively at -30°C for 1 hours, and the temperature was elevated spontaneously to room temperature, thereby anionizing the bis(indenyl)ethane. Separately, a nitrogen-purged 200 ml glass flask was charged with 60 ml of THF, and the flask was cooled to below -60°C, followed by gradual
35 addition of 6.7 g of HfCl_4 (which contained 0.78% by weight of zirconium atoms as contaminants). Thereafter, the flask was heated-up to 60°C and stirred for 1 hour. To the flask was added dropwise the anionized ligand, and stirred at 60°C for 2 hours, followed by filtration with a glass filter. The filtrate was concentrated at room temperature to about 1/5 of the original volume. By this operation, solids were separated. The separated solids were filtered with a glass
40 filter, followed by washing with hexane/ethyl ether and vacuum drying to obtain ethylenebis(indenyl)hafnium dichloride.
[0077] The hafnium compound thus obtained contained 0.40% by weight of zirconium atoms.

(Polymerization)

45 [0078] A mixed gas composed of 96.7 mol% of propylene, 2.1 mol% of 1-butene and 1.2 mol% of ethylene was prepared.

[0079] A thoroughly nitrogen-purged 2 liter stainless steel autoclave was charged with 500 ml of toluene and then cooled to 0°C, and the autoclave was further charged with 3 moles of the mixed gas prepared above and 5 mg atom in terms of Al atom of methylaluminoxane. The temperature in the polymerization system was elevated to 45°C, and
50 1.25×10^{-3} mole of the ethylenebis(indenyl)hafnium dichloride obtained as above was added to the system to initiate polymerization at 50°C for 0.5 hours. The polymerization was stopped by the addition of methanol to the polymerization system. The polymer slurry obtained was poured into large amounts of methanol, the slurry was recovered by filtration and washed with an isobutyl alcohol/hydrochloric acid solution to remove the catalyst components therefrom. The recovered polymer was then vacuum dried overnight at 80°C and 26.7 to 40.0 KPa (200 to 300 mmHg) to obtain 51.3
55 g of a polymer having a 1-butene content of 1.4 mol%, the ethylene content of 1.1 mol%, $[\eta]$ of 3.32 dl/g as measured in decalin at 135°C, a melting point of 121°C as measured by DSC, a boiling trichloroethylene-insoluble content of 0% by weight, a boiling n-pentane-soluble content of 0.9% by weight and \bar{M}_w/\bar{M}_n of 2.45 as measured by GPC.

Example 2

[0080] The polymerization was carried out in the same manner as in Example 1 except that the mixed gas composed of 95.1 mole of propylene, 3.9 mol% of 1-butene and 1.0 mol% of ethylene was used to obtain 48.5 g of a polymer having the 1-butene content of 2.7 mol%, the ethylene content of 0.8 mol%, $[\eta]$ of 3.29 dl/g, a melting point of 118°C, a boiling trichloroethylene-insoluble content of 0% by weight, a boiling n-pentane-soluble content of 1.1% by weight and \bar{M}_w/\bar{M}_n of 2.40.

10 **Claims**

1. A propylene random copolymer comprising structural units (a) derived from propylene, structural units (b) derived from ethylene and structural units (c) derived from α -olefin of 4 to 20 carbon atoms, and having

- 15 (i) the structural units (a) in an amount of 90 to 99 mol%, the structural units (b) in an amount of 0.5 to 9.5 mol% and the structural units (c) in an amount of 0.5 to 9.5 mol%,
 (ii) an intrinsic viscosity $[\eta]$ as measured in decalin at 135°C of 0.5 to 6 dl/g,
 (iii) a melting point $[T_m]$ as measured by a differential scanning calorimeter falling within the range of

$$20 \quad 70 < T_m < 155 - 5.5 (100 - P)$$

wherein P is the propylene content (mol%) present in the copolymer, and
 (iv) a boiling trichloroethylene-insoluble content of less than 5% by weight.

- 25 2. A process for preparing propylene random copolymers as claimed in claim 1, which process comprises copolymerizing propylene, ethylene and an α -olefin of 4 to 20 carbon atoms in the presence of a catalyst comprising

30 [A] a hafnium compound having as a ligand a multidentate compound in which at least two groups selected from among cycloalkadienyl groups or substituted groups thereof are linked together via ethylene groups, and [B] an organoaluminum oxy-compound.

3. A heat sealing agent comprising the propylene random copolymers as claimed in claim 1.

35 **Patentansprüche**

1. Statistisches Propylen-Copolymer, umfassend von Propylen abgeleitete Struktureinheiten(a), von Ethylen abgeleitete Struktureinheiten (b) und von α -Olefin abgeleitete Struktureinheiten (c) mit 4 bis 20 Kohlenstoffatomen; und aufweisend

40 (i) die Struktureinheiten (a) in einer Menge von 90 bis 99 Mol-%, die Struktureinheiten (b) in einer Menge von 0,5 bis 9,5 Mol-% und die Struktureinheiten (c) in einer Menge von 0,5 bis 9,5 Mol-%,

45 (ii) eine Eigenviskosität $[\eta]$, wie in Decalin bei 135°C gemessen, von 0,5 bis 6 dl/g,

(iii) einen Schmelzpunkt $[T_m]$, wie durch ein Differentialabstastkalorimeter gemessen, innerhalb eines Bereichs von

$$50 \quad 70 < T_m < 155 - 5.5 (100 - P)$$

wobei P der Propylengehalt (Mol-%) in dem Copolymer ist, und

55 (iv) einen unlöslichen Gehalt in siedendem Trichlorethylen von weniger als 5 Gew.-%.

2. Verfahren zur Herstellung von statistischen Propylencopolymeren gemäß Anspruch 1, wobei das Verfahren die Copolymerisierung von Propylen, Ethylen und einem α -Olefin von 4 bis 20 Kohlenstoffatomen in Gegenwart eines

EP 0 769 505 B1

Katalysators umfaßt, umfassend:

5 [A] eine Hafniumverbindung mit einer Multidentatverbindung als Ligand, in welcher mindestens zwei Gruppen, ausgewählt aus Cycloalkadienylgruppen oder substituierten Gruppen davon, über Ethylengruppen miteinander verbunden sind, und

[B] eine Organoaluminiumoxyverbindung.

10 3. Heißsiegelungsmittel, umfassend die statistischen Propylencopolymere gemäß Anspruch 1.

Revendications

15 1. Copolymère statistique à base de propylène comprenant des motifs constitutifs (a) dérivés de propylène, des motifs constitutifs (b) dérivés d'éthylène et des motifs constitutifs (c) dérivés d'une α -oléfine comportant de 4 à 20 atomes de carbone, et présentant

20 (i) de 90 à 99 % en moles de motifs constitutifs (a), de 0,5 à 9,5 % en moles de motifs constitutifs (b) et de 0,5 à 9,5 % en moles de motifs constitutifs (c),

(ii) une viscosité intrinsèque $[\eta]$, mesurée dans la décaline à 135 °C, de 0,5 à 6 dl/g,

(iii) un point de fusion (T_m), mesuré par analyse calorimétrique différentielle, compris dans la fourchette

$$70 < T_m < 155 - 5,5 (100 - P)$$

25

où P représente la teneur en propylène (en % en moles) présente dans le copolymère, et

(iv) une teneur en matières insolubles dans du trichloroéthylène à ébullition inférieure à 5 % en poids.

30 2. Procédé pour préparer des copolymères statistiques à base de propylène selon la revendication 1, lequel procédé comprend la copolymérisation de propylène, d'éthylène et d'une α -oléfine comportant de 4 à 20 atomes de carbone en présence d'un catalyseur comprenant :

35 [A] un composé d'hafnium ayant comme ligand un composé multidenté dans lequel au moins deux groupes choisis parmi les groupes cycloalkadiényle ou leur groupes substitués sont reliés ensemble par l'intermédiaire de groupes éthylène, et

[B] un composé oxy-organoaluminique.

40 3. Agent d'étanchéité à chaud comprenant des copolymères statistiques à base de propylène selon la revendication 1.

45

50

55

FIG. 1

(A) Transition metal component

Hafnium compound having as a ligand a multidentate compound in which at least two groups selected from among conjugated cycloalkadienyl groups or substituted groups thereof are linked together via ethylene groups, or a treated product thereof.

(B) Organometallic component

Organoaluminum oxy - compound

Olefin copolymer

FIG. 2

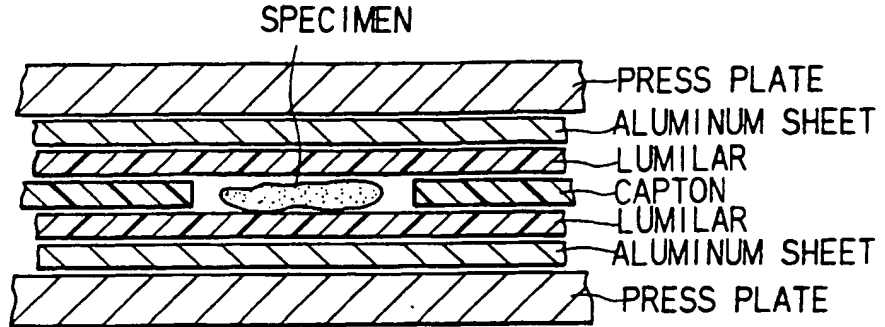


FIG. 3

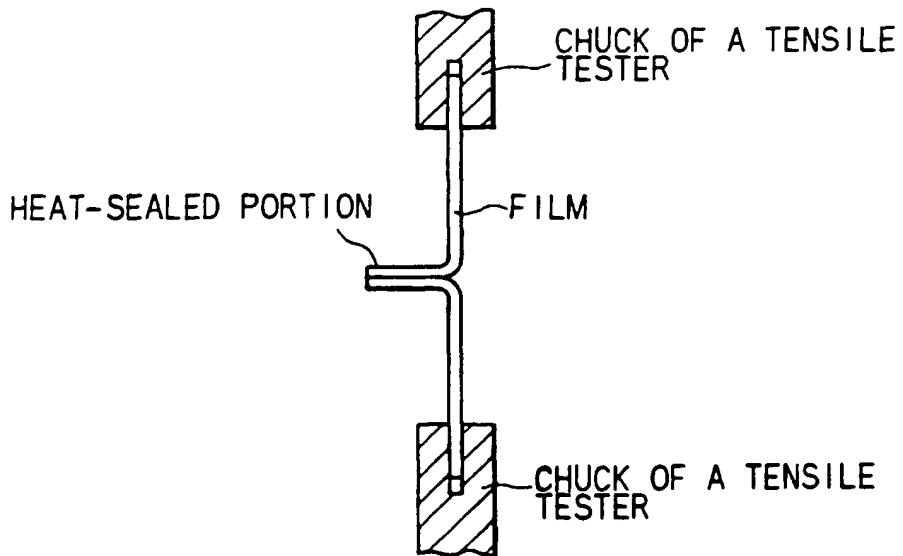


FIG. 4

